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IMPROVED IONIZATION CROSS-SECTION DETECTORS

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J. E. Lovelock, G. R. Shoemake, and A. Zlatkis

Department of Chemistry, University of Houston, Houston, Texas

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Abstract

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The ionization cross-section detector is recognized as one of the few unequivocal detection devices available for use in gas chromatography. The use of an integral pair ionization cross-section detector makes it possible to utilize the desirable characteristics associated with this detection method at reduced pressures, for programmed temperature and pressure (or flow programmed operation) without the accompanying deficiencies often encountered with other detection systems. A micro cross-section detector has been developed with a total volume of 8 microliters. This cell is used to provide cross-section responses for components emerging from 0.01 inch diameter capillary chromatographic columns, thus extending the range of application of ionization cross section. The foregoing detectors are readily adaptable to the constraints imposed on a flight model chromatograph for interplanetary exploration. The value Q, the cross section for ionization for elements, can be experimentally determined and calculations applied that allow the determination of the mass of component represented by any chromatographic peak.

Author

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IMPROVED IONIZATION CROSS-SECTION DETECTORS

The ionization cross-section detector of Pompeo and Otvos (5) has long been recognized as a close approach to the ideal detector for gas chromatography. The disadvantages in the original version were a poor sensitivity, detectivity and the fact that its ionization source was frequently strontium-90, a radio-nucleide of such notoriety that its use could generate apprehension and administrative problems. The introduction of tritium as the radiation source in a recent improvement in design as reported by Lovelock, Shoemake and Zlatkis (3) has obviated the disadvantages associated with the use of strontium-90. An improvement in sensitivity of two orders of magnitude was achieved by a detector configuration in which a high intensity of ionization was delivered to a small volume of gas.

The development of an improved ionization cross-section detector was stimulated by a practical need for a rugged reliable and reproducible detection system for the proposed planetary atmosphere measurements of the National Aeronautics and Space Administration. This stimulus has continued and the account that follows is of the recent advances in the theory and practice of ionization cross-section detectors. In particular, a detector with a sensing volume of only 8 microliters with an even higher sensitivity to small masses is described as well as an integrated pair of detectors arranged to provide compensation for large changes in the ambient temperature, pressure and composition of the carrier gas. The absolute characteristics of the ionization cross-section detector, briefly reported by Simmonds and Lovelock (6) are also considered.

Procedure

Physical Basis

The general physical basis of ionization cross-section measurements in chemical analysis has been comprehensively described by Otvos and Stevenson (4).

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The physical principles on which the recent improved detectors are based are as follows: The number of ion pairs (i) produced per unit length of travel of a β particle of known energy through a gas at S.T.P. is given by,

$$i \propto Q \qquad (1)$$

where Q is the cross section for ionization of the gas under consideration. When, n, particles traverse the gas in unit time the rate of ion production is, ni, and under practical conditions this rate of ion production can be accurately measured by the flow of current (I) associated with their collection at a charged electrode. This may be expressed as

$$I \propto ni \propto nQ \qquad (2)$$

With any gas the rate of ion production due to a steady irradiation with particles of known energy is determined by the length of the radiation path, the ambient physical variables of temperature (T), pressure (P), and the molecular ionization cross section of the gas (Q). If the gas is assumed to have ideal properties and the energy of the radiation is known and only a small portion of it is absorbed in the gas; then with a given path length and temperature the rate of ion production or current, as shown above, is uniquely determined by the gas pressure. Similarly the ionization cross section is a constitutive property and therefore is a mixed gas the current is determined by the sum of the molar fractions (Xi) and ionization cross sections of the components of the mixture (Qi), so that

$$I = \frac{nPV}{RT} \sum XiQi \qquad (3)$$

In a practical ionization cross section detector these ideal conditions are closely approached. The mixture of low molecular weight carrier gas and dilute vapor can without appreciable error be considered as an ideal gas and the ambient physical variables experimentally determined. The only point at which the device fails to achieve absolute status in a physical sense is where the atomic ionization

cross-sections are considered. These are dependent upon the energy of the β particles. With practical radioactive sources there is a wide distribution of β particle energies partly because of the physics of decay and partly due to energy absorption in the material of the source. The atomic ionization cross-sections do not vary much for β particles with energies above 1 K ev and the mean energy of β particles from a given radioactive source is substantially consistent. In the important practical sense, the detector is absolute.

It has been shown (4) that the molecular ionization cross section is a constitutive property and is equal to the sum of the atomic ionization cross-sections of the atoms of the molecule. This fact coupled with the previous remarks give rise to an important but comparatively unknown quality of the ionization cross-section detector; it is absolute in the sense that the mass of a known substance appearing as a peak on a chromatogram can be calculated from constitutive properties of the elements of the molecule and ambient physical conditions. Calibration is not required at any step. The ionization cross-section detector is the only practical gas chromatography detector with this desirable quality. Even the gas density balance as ordinarily used requires the calibration of its anemometer. The physical basis of absolute measurements with ionization cross section detectors and the derivation of a practical expression relating the peak area of a known substance to its mass are as follows: For an integral pair detector or plane parallel design containing two equivalent radioactive sources,

$$I = \frac{KPV}{RT} \sum X_i Q_i \qquad (4)$$

where K is a cell constant including n from equation (3) and in addition is dependent on cell geometry.

In practice the current associated with pure carrier gas is offset and only the signal due to the presence of test substance is observed. In this instance the

current change, ΔI, accompanying the presence of a vapor concentration X is

$$\Delta I = \frac{KPV}{RT} \, X \, (Qx-Qc) \qquad (5)$$

Figure 1 is a diagramatic representation of a chromatographic peak where I_o is the standing current, ΔI the current change associated with the presence of test substance, I_s the total current, Δt the time of elution of the chromatographic peak, A_2 the area of the peak and A_1 the area of a segment beneath the standing current plateau. The value for the cell constant K is determined from the area A_1 and is found to be

$$K = \frac{RTI_o}{PVQc} \qquad (6)$$

where Qc is the cross section for ionization of the carrier gas. The area A_2 of the chromatographic peak will be given by

$$A_2 = \frac{\Delta I \Delta t}{2} \qquad (7)$$

Substitution of the proper expression for ΔI and K yields an expression for the molar fraction of test substance present

$$X = \frac{2A_2 Qc}{I_o \Delta t (Qx-Qc)} \qquad (8)$$

where Qx is the ionization cross section of the test substance. With the proper considerations a value is obtained for the mass of substance (M_s) represented by a chromatographic peak which is

$$M_s = \frac{2PF \Delta t Z_x A_2 Q_c}{RTI_o \Delta t (Qx-Qc)-2A_2 Q_c} \qquad (9)$$

A somewhat easier approach is allowed when the molar fraction of test substance is less than 1% of the carrier gas in which case equation (9) reduces to

$$M_s = .244 \, \frac{PFZ_x A_2 Qc}{TI_o(Qx-Qc)} \qquad (10)$$

where the additional term F is equal to the flow rate of carrier gas measured at the detector outlet at the temperature of operation and Z_x is the molecular weight of the test substance.

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Automatic Compensation

The sensitivity of the ionization cross-section detector to changes in the ambient temperature or pressure is sufficiently low for a single uncompensated detector to meet the needs of routine isothermal gas chromatography. When the temperature, pressure or composition of the carrier gas in the detector is subject to large changes; for example in temperature programmed gas chromatography, or in the sampling of a planetary atmosphere by a descending probe, a pair of identical detectors can be used in a circuit design to compensate against drift of the base line or false signals from unknown changes in the ambient variables. The notion of compensation using a pair of identical detectors was introduced early in the history of ionization cross-section detectors by Boer (2) and has been recently demonstrated by Abel and de Schmertying (1). The theory and practice of compensation, particularly where large changes in gas pressure are to be cancelled have not been previously described.

Figure 2 shows the two possible circuit arrangements for a balanced pair of detectors. In the parallel arrangement of Fig. 2 A a perfect balance under almost all conditions is readily achieved. Small differences between the standing currents of the two detectors under otherwise identical conditions can be cancelled by equivalent changes in the individual resistors, R_i, in series with the detectors. With both detectors the current flows which are compared come from the collection of the same species of charge carriers which may be either negative or positive. In spite of these apparent desirable features the parallel balance circuit is somewhat impractical because of the inherent high impedance of ionization detectors. The arrangement shown in Figure 2 A would require an electrometer with both sides of the input floating or, alternatively, two electrometers with the signal comparison made at low impedance outputs which is of course expensive.

The series balanced circuit of Figure 2 B is more practical and requires only one conventional electrometer. Its disadvantages are that balancing must be done by the tedious initial adjustment of the radioactive source intensities when the detectors are evacuated and subsequently balancing the pair by small changes in the cell geometry of one of the detectors. These problems arise from the comparison of negative charge carriers in one detector with positive charge carriers in the other. Since the consequences of this are important in the practical use of the balanced pair of detectors the physical basis will be discussed.

Consider a simple ion chamber connected to a source of potential and to the input resistance of an electrometer (R_1), as shown in Figure 3. If the chamber is evacuated and a radiation source is attached to either of the chamber electrodes a potential will be observed across R_1. The polarity of this potential depends only upon the site of the radiation source and is independent of the polarity of the potential applied to the chamber. The origin of this potential is the separation of charges which always occurs with β decay. If the source is attached to electrode (A) a negative potential will appear at (B) due to the arrival of the β particles at that electrode. If the source is at (B) a positive potential will appear from the positive charged recoiling nuclei left imbedded in the metal of the radiation source.

When the chamber contains gas a number of ion pairs (Y) is produced by each β particle as it traverses the chamber. The current flow in the resistance R_1 due to the collection of these ions by an appropriate applied potential at the chamber electrodes will be in a direction determined by the polarity of the applied potential. The total current flow due to both the ionization of the gas and to primary particle collection will be

$$I = n \, (Y \overset{+}{_-} 1)$$

where n is the β particle flux per second. When the primary and secondary charge

carriers arriving at electrode B are of the same sign the current is n(Y + 1) and when they are of the opposite sign, n(Y - 1). In a detector containing only a single radioactive source equation (9) becomes

$$M_s = \frac{2PF \Delta t Z_x A_2 Q_c}{RT(I_0 \Delta t \pm n \Delta t)(Q_x - Q_c) - 2A_2 Q_c} \quad (11)$$

and equation (10) becomes

$$M_s = .244 \frac{PFZ_x A_2 Q_c}{T(I_0 \pm n)(Q_x - Q_c)} \quad (12)$$

It might appear that unwanted current flow due to the primary charge separation could be avoided by an external source of radiation. In practice however, the additional complications in design are more onerous than the offsetting of the primary current flow. The single channel detector previously described (2) employs a radiation source at each electrode. Under these circumstances the primary currents cancel which is an additional previously unmentioned virtue of this design.

When the balanced pair systems shown in Figure 2 are used and the radiation sources attached to the electrodes indicated, the primary current is again cancelled and the signal current is solely from ion production in the gas. Failure to observe the correct site and polarity of the radiation sources with the balanced pair detectors can give rise to erroneous and even negative signals for a change in gas composition.

Construction

Figure 4 shows the dimensions and materials of construction of a 8 microliter total volume ionization cross-section detector. The ion chamber is formed from 1.6 mm diameter tubing which encloses the radiation source. The source is a sheet of stainless steel foil .002 inches thick with a surface layer of 200 millicuries titanium tritide. The collecting electrode, made of 0.8 mm diameter stainless steel rod, is mounted axially along the chamber. Carrier gas enters the

chamber through channels in a plug of teflon which also serves to insulate and support the ion collecting electrode. The gas exit is through a central channel in a second teflon plug through which the ion collecting electrode extends for exterior electrical connection.

Figure 5 shows the dimensions and materials of construction of a compensated pair ionization cross section detector. In this construction the two ion chambers are integrally connected and mounted within a single external body. The common ion collecting electrode is an axial rod in the left chamber and the inner cylindrical wall of the right chamber of the pair. The rod section is hollow and serves to conduct the gas from the chamber and also, where it extends through a teflon bushing in the outer metal body of the detector, as an external electrical connection to the electrometer. At the end of the left chamber the axial rod passes through teflon insulation and expands to form the second ion chamber. Gas enters this ion chamber through another axial rod which also serves as the external connection to the negative supply of potential. This rod is threaded where it passes through an insulated supporting metal plate. This provides a fine adjustment of the volume of the right chamber so that the final electrical balancing can be made with the detector assembled. The external supporting metal case also functions as the second electrode of the left chamber to which is connected the positive supply of potential. The radiation sources are again stainless steel foils with a layer of titanium tritide on the surface. They are mounted on the inner surfaces of the outer walls of both ion chambers.

Performance Measurement

The performance of the 8 microliter volume detector was measured using the same apparatus and procedure as that previously described (3) with the 80 microliter volume detector. Briefly this was done by connecting the detector to a logarithmic dilution vessel filled with test gas. The concentration of this gas

was continuously diluted by a constant known flow of carrier gas into the vessel and the detector signal monitored during the period the test gas concentration decayed from 100% to that at which the detector signal was at or near the noise level. The practical performance of the detector was also observed when it was used to monitor the effluent from 0.01 inch diameter capillary columns.

The characteristics of the balanced pair detector at S. T. P. were measured as before using the logarithmic dilution method. The experimental arrangement is shown in Figure 6. However, this detector was designed for use at pressures considerably different from atmospheric, i.e., in the range 5 to 250 mm Hg. Low pressure measurements of the detector performance were made using the apparatus illustrated in Figure 7. The detector was mounted within a plexiglass vacuum desiccator which was connected to a vacuum pump through a buffer storage volume, to reduce fluctuations, and to an accurate absolute pressure indicator. When the detector was tested using a dilution vessel the vessel was operated at atmospheric pressure and a small portion of the effluent from the vessel passed through a capillary restriction into the vacuum chamber. All necessary gas and electrical connections were made by passing such connections through the desiccator walls and sealing with an epoxy resin. When the detector was tested at the effluent of a gas chromatographic column these were usually included with the detector inside the vacuum vessel.

Figure 8 shows the experimental arrangement used when the balanced pair detector is operated in the standard mode. Figure 9 illustrates the recommended experimental method for the balanced pair detector when used for temperature programming or dual parallel column operation. For parallel column application the sample injection is at point (J), while for temperature programming the sample is injected at point (B).

Though not desirable in most instances as parallel column operation, a series column arrangement may be used as illustrated in Figure 10. In either the parallel or series column application care must be exercised in column choice so that sample components do not arrive in both cells simultaneously as one of the pair must be available to serve as a reference.

Results and Discussion

Table I lists the performance characteristics at S. T. P. for both detectors. The characteristics for the previously described 80 microliter volume detector (1) are also included for comparison. The detectivities are expressed as the static concentration parameter gm per ml, which is to be the same for all three detectors, and as the much more useful dynamic parameters apparent ionization efficiency and in units gms per sec, at an operating time constant of one second. We do not apologize for wishing to include the sensitivities of these concentration measuring detectors in the dynamic units mass per unit time for a stated volumetric time constant. The gas chromatograph is a dynamic method of analysis and when detector capability and comparison are considered, the dynamic mass transfer expression, mass or moles per unit time at unit operating time constant is a convenient single parameter. For the three detectors listed in Table I the sensitivities in the mass units are seen to improve as the volume of the detector is reduced. With the 8 microliter volume detector the least detectable mass appearing as a five second wide peak on a capillary column would for example be in the region of 0.1 to 0.5 nanograms. The other performance and operating characteristics listed in Table I are less controversial and for the most part self-explanatory.

The potentialities of the 8 microliter volume detector are perhaps best illustrated by the chromatogram Figure 11 made with a 0.01 inch diameter capillary column. The optimum flow rate with such columns is in the region of 16 microliters per second so that the operating time constant of the detector is

only 0.5 seconds. This is fast enough for nearly all of the practical needs of

gas chromatography. Where faster analysis are contemplated even shorter operating

time constants are possible by an increase in gas flow through the detector. This

may however require a price to be paid in terms of resolution or sensitivity.

The ionization processes within the detector are in gas chromatography terms

instantaneous so that the time constant is uniquely determined by the detector

volume and the gas flow rate.

Figure 12 is an illustration of a chromatogram obtained with the balanced

pair detector utilizing the parallel column operation previously discussed.

Figure 13 shows a similar analysis carried out with the balanced pair detector

operating with the columns in series.

To illustrate the usefulness of the balanced pair detector in temperature

programming, a chromatogram, Figure 14 A, was obtained showing a complex hydro-

carbon mixture. The deviation of the base line due to bleeding of the liquid'

substrate becomes quite apparent and calculation of peak areas made somewhat

difficult. Figure 14 B shows the identical analysis made with the balanced

pair detector utilizing the temperature programmed mode of operation. No shift

in baseline is observed due to loss of liquid substrate from the column. Any

temperature change on the detector itself is found to have negligible effect

on the baseline since a change of 200°C on the detector resulted in a net baseline

shift of less than 3% of full scale deflection. This minor change due to detector

characteristics would be obviated if the cells were exactly balanced as previously

described.

Figure 15 shows the extent to which the balanced pair detector fails to

achieve a complete cancellation of the signals due to pressure changes. Ideally

this residual error signal should vary linearly with the pressure change. In

practice where the change is large, for example a pressure change from 760 mm Hg

to 20 mm Hg, the effects shown in Figure 15 may occur.. That these are attributable

to differences between the mean energies of the β particles from the two sources is shown by the effect of exchanging the sources between the two chambers (dotted line). This effect is not a serious source of error for the error signal is only one per cent of the standing current at the worst point of the pressure change between 760 mm Hg and 20 mm Hg. It is however worthwhile ensuring that the tritium sources are as similar as possible.

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(2) Boer, H., "Vapor Phase Chromatography", D. H. Desty, ed., Vol. I, Butterworths, London, 1957.

(3) Lovelock, J. E., Shoemake, G. R. and Zlatkis, A. Anal. Chem. <u>35</u>, 460 (1963).

(4) Otvos, J. W., Stevenson, D. P. J. Am. Chem. Soc., <u>78</u>, 546 (1956).

(5) Pompeo, D. J., Otvos, J. W. (to Shell Development Co.), U. S. Patent 2,641,710 (1963).

(6) Simmonds, P. G. and Lovelock, J. E. Anal. Chem. <u>35</u>, 1345 (1963).

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LEGENDS TO FIGURES

(1) Diagramatic representation of an eluted chromatographic peak

(2) Two modes of operation of a balanced pair ionization cross-section detector

(3) Basic circuit of an ionization cross-section detector system

(4) 8 microliter volume cross-section detector

(5) Balanced pair ionization cross-section detector

(6) Experimental arrangement for investigation of operating characteristics
of the balanced pair ionization cross-section detector: A = carrier gas
supply, B = gas tee, C = sample supply, D = three way valve, E = logarithmic
dilution vessel, F & G = polarizing potential, H = detector, I = electrometer,
J = recorder

(7) Experimental arrangement for investigation of detector performance under
reduced pressure: A = vacuum pump, B = atmospheric bleed, C = buffer tank,
D = pressure indicator, E = vacuum vessel

(8) Experimental arrangement for single column operation of the balanced pair
ionization cross-section detector: A = carrier gas supply, B = sample inlet,
C = column, D & E = polarizing potential, F = detector, G = electrometer,
H = recorder

(9) Experimental arrangement for parallel column operation or temperature program
operation of the balanced pair ionization cross-section detector: A = carrier
gas supply, B = sample inlet for temperature program, C_1 & C_2 = columns,
D = oven, E & F = polarizing potential, G = detector, H = electrometer,
I = recorder, J = sample inlet for parallel column operation

(10) Experimental arrangement for series column operation of the balanced pair
ionization cross-section detector: A = carrier gas supply, B = sample inlet,
C_1 & C_2 = columns, D & E = polarizing potential, F = detector, G = electrometer,
H = recorder

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(11)   Chromatogram obtained with 8 microliter volume ionization cross-section
        detector.   Column 200 ft 0.01 inch dimethyl sulfolane, carrier gas =
        hydrogen, inlet pressure = 30 psig, temperature = 25°C, sample =
        5 microliters petroleum ethyl vapor

(12)   Chromatogram illustrating parallel column operation of the balanced pair
        ionization cross-section detector.   Column 1 = 3 ft 1/8 inch diameter
        packed with 5 A molecular sieve; Column 2 = 6 inch 1/8 inch diameter packed
        with silica gel; Carrier gas = hydrogen; inlet pressure = 20 psig;
        temperature = 25°C; Sample size = 100 microliters

(13)   Chromatogram illustrating series column operation of the balanced
        pair ionization cross-section detector.   Column 1 = 6 inch 1/8 inch
        diameter packed with silica gel; Column 2 = 3 ft 1/8 inch diameter packed
        with 5 A molecular sieve; Carrier gas = hydrogen; inlet pressure =
        20 psig; temperature = 25°C; sample size = 250 microliters.

(14)   Chromatograms illustrating temperature program operation of the balanced
        pair ionization cross-section detector

(15)   Effect of pressure on the response of the balanced pair ionization cross-
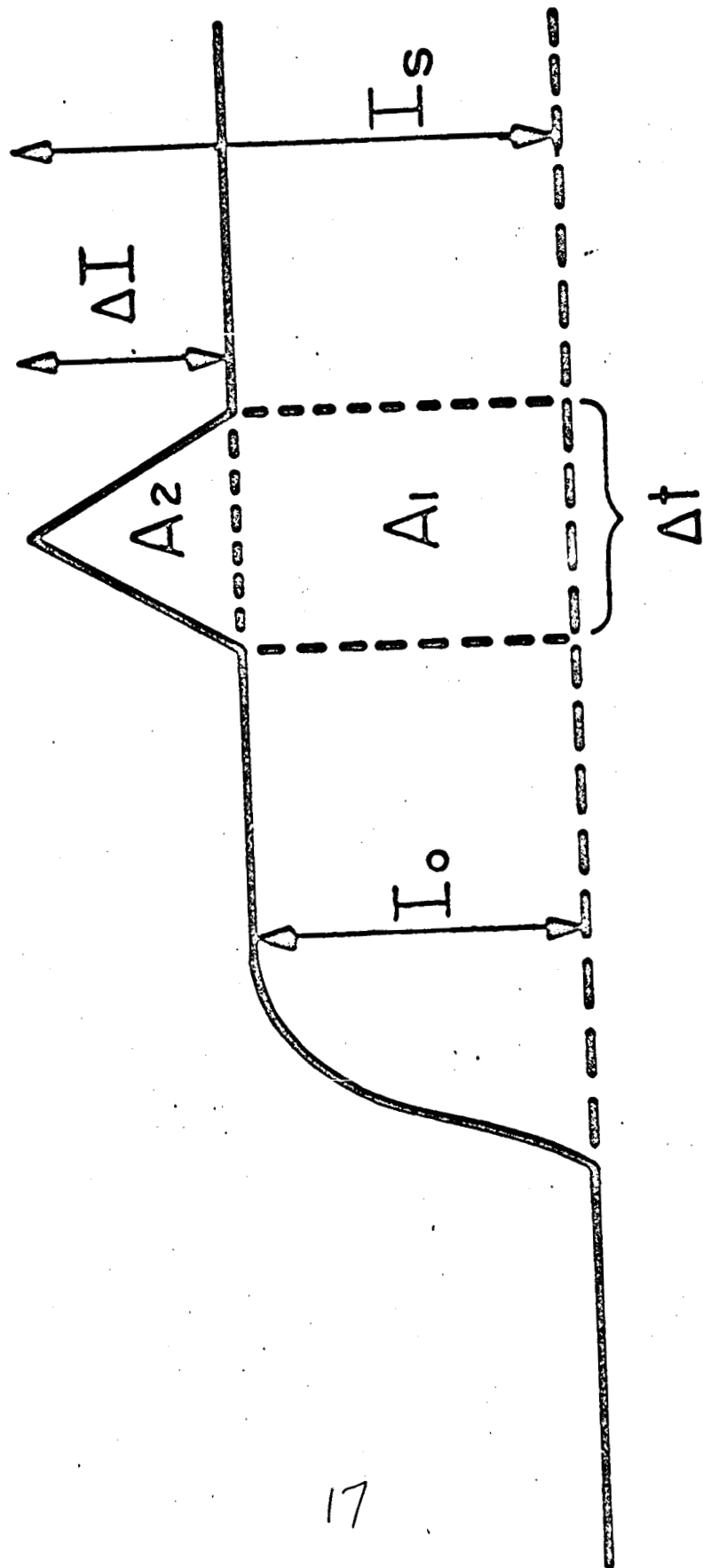   section detector

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TABLE I. PERFORMANCE CHARACTERISTICS OF DUAL
IONIZATION CROSS-SECTION DETECTOR COMPARED WITH
THOSE OF PREVIOUS IONIZATION CROSS-SECTION DETECTORS

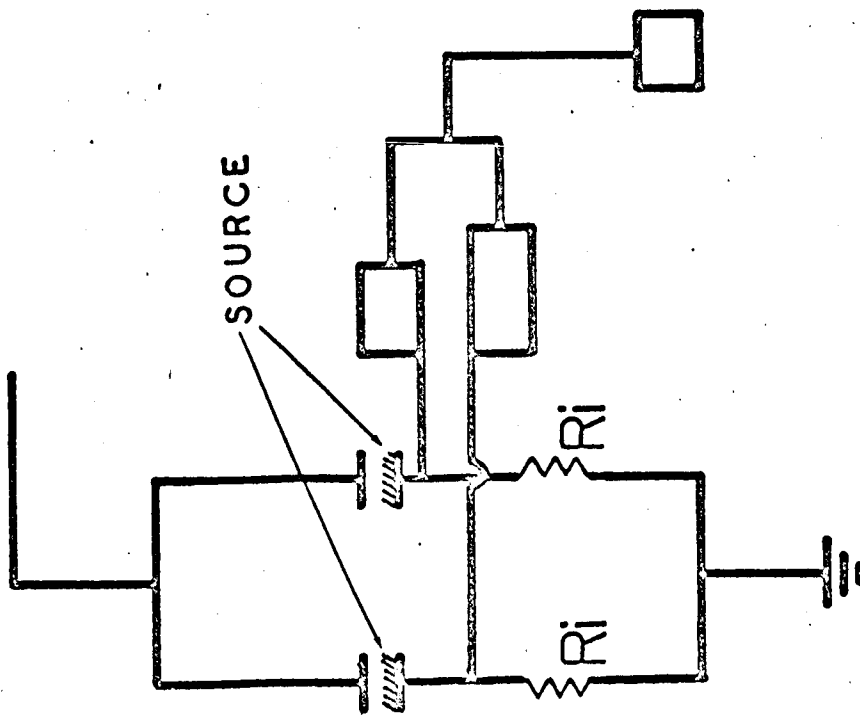(MEASUREMENTS MADE WITH A BAND PASS OF 0 TO 1 CYCLE PER SECOND)

CHARACTERISTIC	BALANCED PAIR** DETECTOR	80 MICROLITER DETECTOR	8 MICROLITER DETECTOR
IONIZATION EFFICIENCY	10^{-8}	$.10^{-7}$	3.7×10^{-7}
LINEAR DYNAMIC RANGE	1.5×10^5	3×10^5	3×10^5
NOISE LEVEL (AMPERE) H_2 OR He-5% CH_4	10^{-13}	10^{-13}	10^{-13}
BACKGROUND CURRENT IN HYDROGEN (AMPERE); PER SINGLE CHANNEL H_2 / He-CH_4	2.5×10^{-8} / 2.5×10^{-8}	5×10^{-9}	1.3×10^{-9}
MINIMUM DETECTABLE QUANTITY (gm. per sec.)*	1.6×10^{-9}	3.2×10^{-10}	3.2×10^{-11}
MINIMUM DETECTABLE CONCENTRATION BY VOL.	3.2×10^{-6}	2×10^{-6}	2×10^{-6}
CARRIER GAS	H_2 or He 5% CH_4	H_2 or He 5% CH_4	H_2 or He 5% CH_4
DETECTOR VOLUME (ml.)	.250	0.08	.008
SUBSTANCES DETECTABLE	ALL	ALL	ALL

*ASSUMING AN OPERATING TIME CONSTANT OF 1 SECOND.
**THESE PARAMETERS DETERMINED AT 760 mm. OPERATION AT 250 mm. WILL PROVIDE AN APPROXIMATE THREE FOLD IMPROVEMENT IN CHARACTERISTICS.
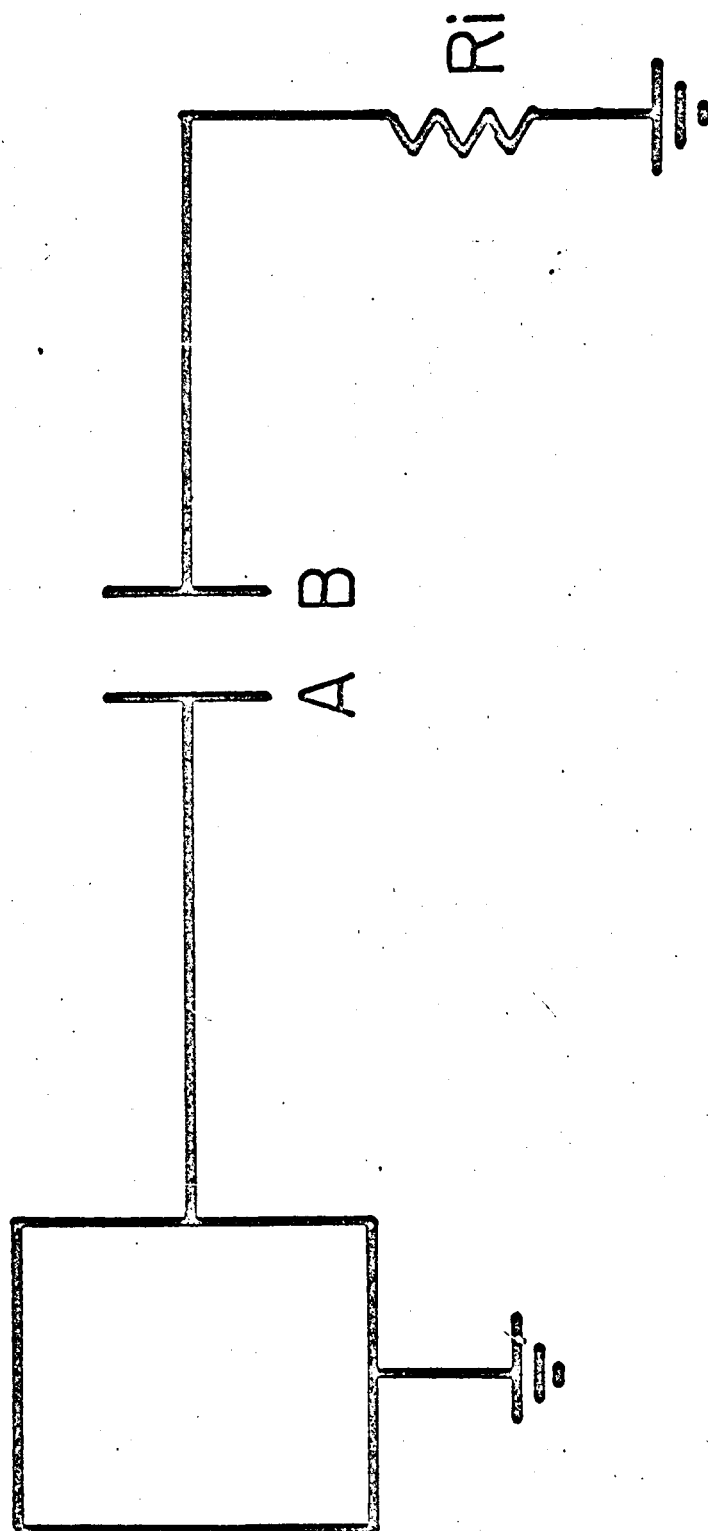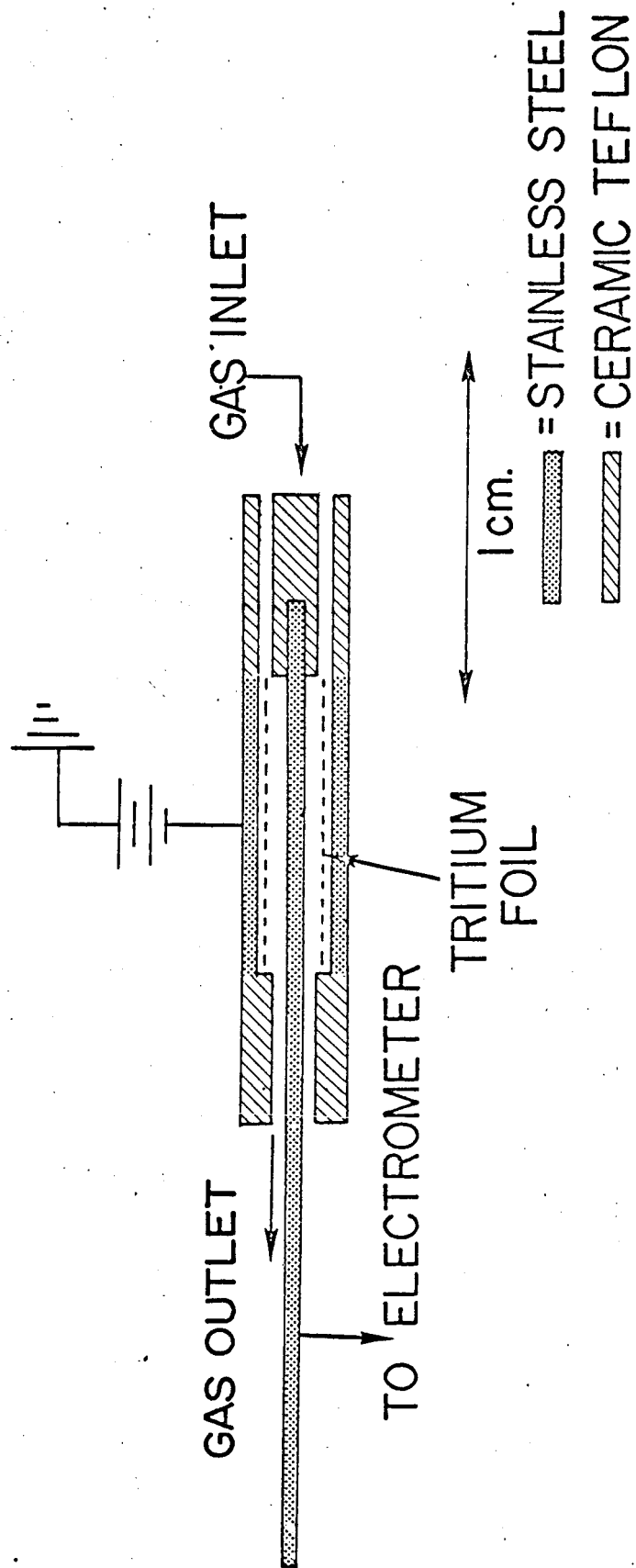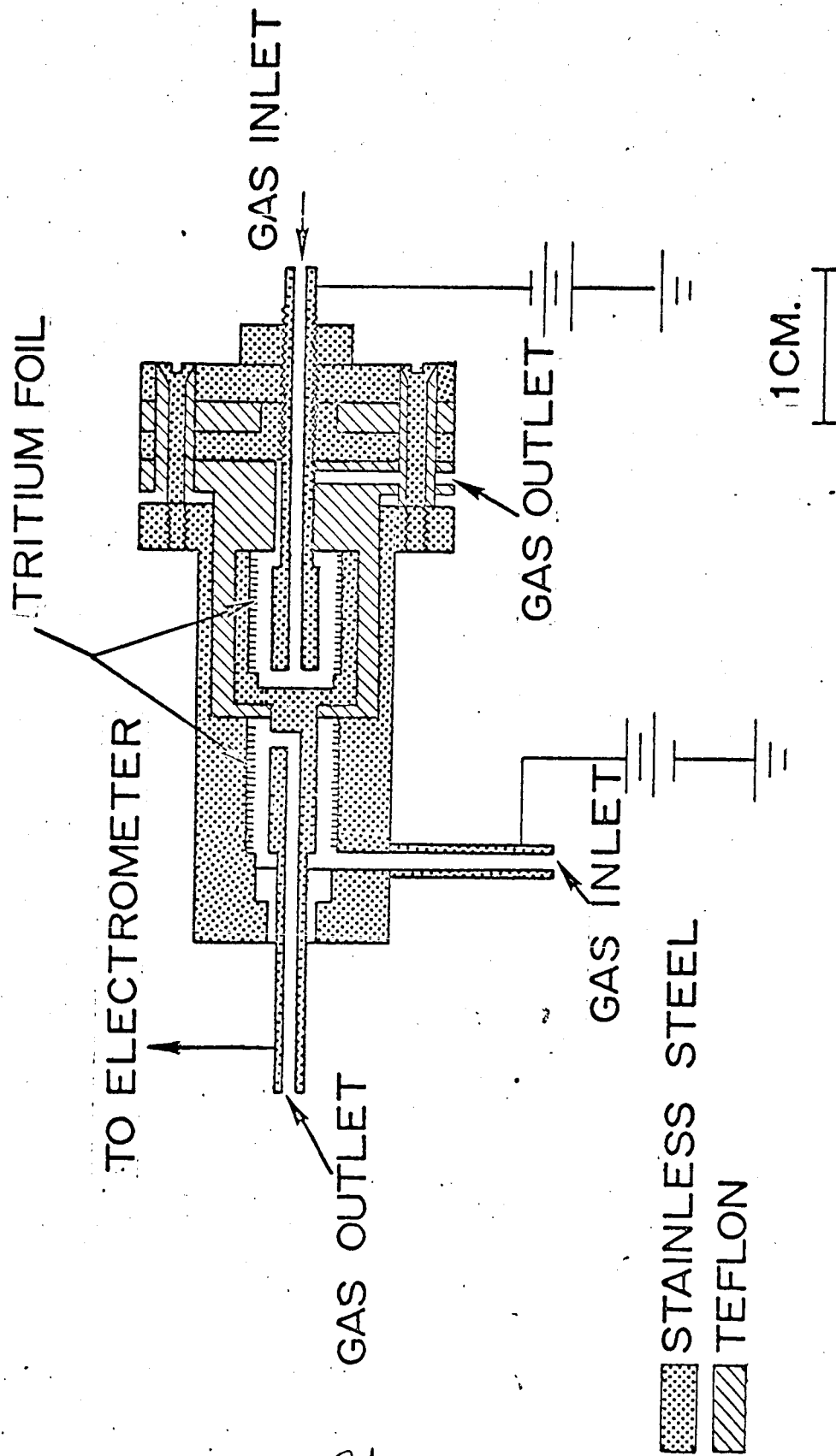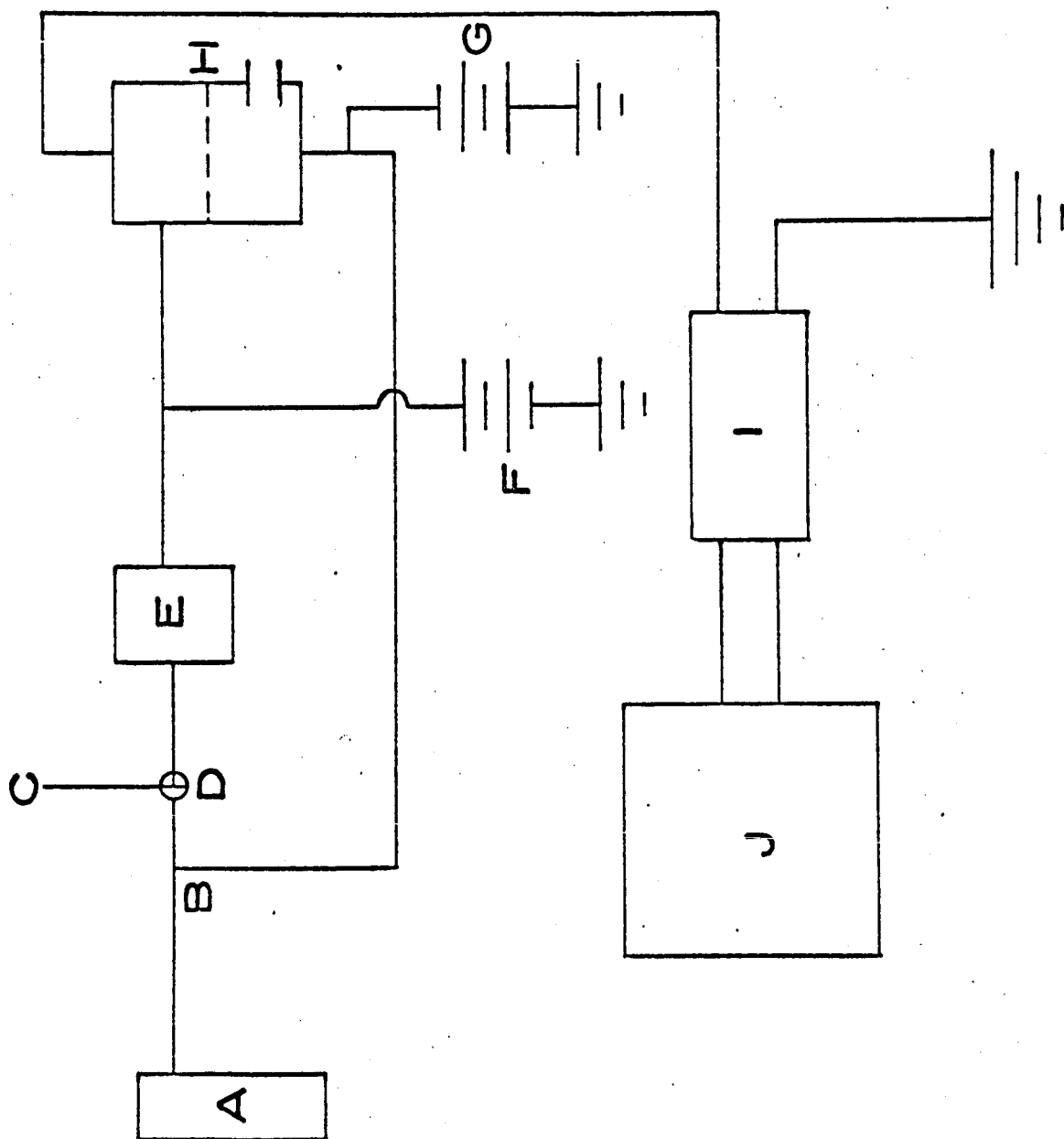
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17

ELECTROMETER

SOURCE

SOURCE OF POTENTIAL

SOURCE

Ri

Ri

A

B

19

SOURCE OF POTENTIAL Pi

A B

Ri

19

GAS INLET

GAS OUTLET

TO ELECTROMETER

TRITIUM FOIL

1 cm.

= STAINLESS STEEL

= CERAMIC TEFLON

20.

GAS INLET

TRITIUM FOIL

TO ELECTROMETER

GAS OUTLET

GAS OUTLET

GAS INLET

1 CM.

STAINLESS STEEL

TEFLON

21

AIR

INJECT

INJECT

COMPOSITE

CO_2

$C_2H_2 (H_2O)$

O_2

N_2

30 SECONDS

28

CH4 N2 O2 INJECT

CO2 COMPOSITE

280 SECONDS

31

PRESSURE, MM Hg

CURRENT, AMPERES X 10⁻¹⁰

.... SOURCE
REVERSED

760

90

20

3

2

1

1

2

3

32